

A Model for the Schottky Anomaly in Metallic $Nd_{2-y}Ce_yCuO_4$

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Abstract

We present a simple model for the doped compound $Nd_{2-y}Ce_yCuO_4$, in order to explain some recent experimental results on the latter. Within a Hartree-Fock context, we start from an impurity Anderson-like model and consider the magnetic splitting of the $Nd-4f$ ground state Kramers doublet due to exchange interactions with the ordered Cu moments. Our results are in very good agreement with the experimental data, yielding a Schottky anomaly peak for the specific heat that reduces its amplitude, broadens and shifts to lower temperatures, upon Ce doping. For overdoped compounds at low temperatures, the specific heat behaves linearly and the magnetic susceptibility is constant. A smooth transition from this Fermi liquid like behavior occurs as temperature is increased and at high temperatures the susceptibility exhibits a Curie-like behavior. Finally, we discuss some improvements our model is amenable to incorporate.

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Schottky Anomalies, Rare Earths, Anderson Model, Cuprate Oxides

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We develop a model for the compound $Nd_{2-y}Ce_yCuO_4$, following both the conjectures and the experimental results as given by [1]. There, a Schottky-like peak in the specific heat curve $C(T)$ was observed. As Ce doping is increased, this peak reduces its amplitude, broadens and shifts to lower temperatures. In the overdoped case, at low temperatures, $C(T)$ behaves linearly and the magnetic susceptibility remains constant. At high temperatures, the former behaves exponentially and the latter in a Curie-like fashion. A large effective mass was inferred and interpreted as a heavy fermion feature. Czjzek et al. [1] interpretation is as follows: the Schottky-like peaks result from the magnetic splitting of the $Nd-4f$ ground state Kramers doublet due to exchange interactions with the ordered Cu moments. Taking at face value their interpretation and data, we develop a simple model for this compound's behavior.

We start with an impurity Anderson-like model [2], within a Hartree-Fock (HF) context, and follow a somehow similar modeling as in [3]. We denote by ε_k and $n_{k\sigma} = c_{k\sigma}^\dagger c_{k\sigma}$ the conduction band dispersion and occupation number operator, respectively. For the undoped case the Fermi level (taken as zero throughout this calculation) lies in the gap below the bottom of the conduction band (the undoped compound exhibits semiconducting behavior and undergoes a metal-insulator transition at $y = 0.13$ [1]). As the system is doped with electrons [4] the band ‘moves’ towards the Fermi level (we assume the metal insulator transition of the band crossing type [5]). In the present modeling, we only consider the doublet f -electron state structure, labeled by the spin variable σ (orbital degeneracy and crystal field effects are neglected at the present time). Let $n_{fi\sigma} = f_{i\sigma}^\dagger f_{i\sigma}$ be the localized f -electron level occupation number, at energy E_o . The f levels are assumed singly occupied (equivalent to consider the f -intra atomic Coulomb term $U_{ff} \rightarrow \infty$). Furthermore we denote by J the exchange interaction between the f and the conduction electrons. The Cu moment coupling via exchange to the f -electrons is modeled in a *non-selfconsistent* fashion, and the Cu moment mean value *times* the exchange constant is denoted by D . Let h be the external magnetic field, and the conduction (c) and f -electron magnetic moment mean values be denoted by $m_{c,f}$, respectively (absorbing all magnetic constants). Finally, the conduction- f electron hybridization is modeled via the Anderson impurity model [2], so the HF Hamiltonian for this model is cast as

$$H = \sum_{k\sigma} E_{k\sigma} n_{k\sigma} + \sum_{i\sigma} E_{f\sigma} n_{fi\sigma} + \frac{V}{\sqrt{N}} \sum_{ki\sigma} \left(c_{k\sigma}^\dagger f_{i\sigma} + f_{i\sigma}^\dagger c_{k\sigma} \right) \quad (1)$$

except for a constant term and where V is the hybridization constant, N the total number of sites, and

$$E_{k\sigma} = \varepsilon_k - \sigma(Jm_f + h) \quad E_{f\sigma} = E_o - \sigma(D + Jm_c + h)$$

Notice the similarity of this Hamiltonian with the one presented by [3] in a related but somehow different context. Following the standard *HF* approach, as given by [2], we obtain the selfconsistent equation for the *f*-moment

$$m_f = -\frac{Im}{\pi} \sum_{\sigma} \sigma \int \frac{d\omega f_T(\omega)}{\omega - E_{f\sigma} + i\Delta(\omega)} \quad (2)$$

with $f_T(\omega)$ the Fermi-Dirac distribution and the *f*-level broadening factor Δ is a function of the energy ω , the hybridization constant V and the conduction electron density of states as given by $\Delta(\omega) = \pi V^2 \rho_c(\omega)$ [2]. Notice the *f*-moment is normalized to the effective moment μ_{eff} [6]. For a wide band metal, Δ is well approximated by its value at the Fermi level. Here, this is not the case since a metal insulator transition occurs as the compound is doped. We approximate Δ by its energy average (around the Fermi level), as $\Delta(\omega) \approx \Delta(y) = \pi V^2 \bar{\rho}_c(y)$. This ‘average’ is a monotonic function of *Ce* doping. The conduction band moment can be likewise approximated as $m_c \approx 2(Jm_f + h)\bar{\rho}_c(y)$. Once the *f*-moment is computed (selfconsistently), we are in a position to compute the *f* contribution to the energy as

$$\mathcal{E} = -\frac{Im}{\pi} \sum_{\sigma} \int \frac{d\omega \omega f_T(\omega)}{\omega - E_{f\sigma}(y) + i\Delta(y)} \quad (3)$$

The specific heat and magnetic susceptibility are readily computed, at zero magnetic field, respectively as

$$\mathcal{C} = \frac{\partial \mathcal{E}}{\partial T} \quad \chi = \left(\frac{\partial m_f}{\partial h} \right)_{h=0} \quad (4)$$

Our results are summarized in the figures. In Figure 1 and 2 we plot the specific heat (in arbitrary units) and the specific heat over temperature, respectively; in Figure 3 the *f* magnetic susceptibility and in Figure 4 the *f* magnetic moment; all versus temperature in log scale. We attempted a quantitative fitting to the specific heat experimental curves [1]. In each Figure we plot four cases, corresponding to the

parameters' configurations (in Kelvin units) listed in the Table, with y the Ce doping relative concentration. The effective mass is estimated via the expression

$$\rho_f(\varepsilon_F \cong 0, T = 0) = \frac{\Delta(y)}{\Delta^2(y) + (D(y) + J(y)m(y))^2}$$

$$\frac{m^*}{m} \cong \frac{2\hbar^2}{ma^2} \rho_f(\varepsilon_F \cong 0, T = 0)$$

where a is the n.n. Nd lattice constant, and taken from [7]. In the last expression we fit the Lorentzian f -broadening with an effective tight binding Hamiltonian density of states.[8]. Furthermore, we consider $E_o - \varepsilon_F \approx 0$ (a non selfconsistent approximation, used in our model to approximately 'force' a singly occupied f -level). The parameters are computed within a virtual crystal approximation scheme [5, 9, 10]. This linear interpolation scheme mimics the effect Ce doping, thus Δ must increase with doping, as electron injection enhances the conduction density of states at the Fermi level. Correspondingly, electron doping must thin down the 'magnetic' parameters D and J , respectively associated to the incomplete filling of the Cu and Nd orbitals.

From Figures 1 and 2 we notice the overall linear behavior of the specific heat at low temperatures, and an exponential behavior at high temperatures, in agreement with the experimental data [1]. Also, as doping (Δ) is increased, the Schottky-like peak moves to lower temperatures, reduces its amplitude and broadens, again in agreement with the experimental data. Notice that within our crude modeling for Δ , a non linear behavior at low temperatures is evident only for near null values of Δ , nevertheless our modeling stands as a good description for the metallic phase of this rare earth compound (this last remark is also valid for the computed susceptibility). $\Delta(\omega, y)$ is a function of both energy and doping, in fact proportional to the conduction band density of states $\rho_c(\omega, y)$. For the undoped case (insulator) $\rho_F = \rho_c(\omega = \varepsilon_F, y) = 0$. As doping is increased, ρ_F becomes finite at the insulator-metal transition. Consider our expression for the specific heat (equations (3) and (4)) with the energy independent approximation $\Delta(y)$. For the case $T \ll \Delta$, the resulting Digamma functions can be expanded (Sommerfeld expansion) rendering the well known linear expression $\mathcal{C} = \gamma T$. On the other hand, for the case $\Delta = 0$ and with $\varepsilon = |E_{f\uparrow} - E_{f\downarrow}|$, it can be readily shown that

$$\mathcal{C} \approx \left(\frac{\varepsilon}{T}\right)^2 \frac{\exp\left(\frac{\varepsilon}{T}\right)}{\left(1 + \exp\left(\frac{\varepsilon}{T}\right)\right)^2}$$

the classical Schottky expression (see for example [11]), with an exponential behavior at low temperatures and a sharp maximum at $T \approx \varepsilon$. So as Δ varies away from zero we expect a transition from an exponential to a linear behavior. Thus, our single particle model accounts for the above mentioned transition as can be inferred from the experimental curves [1]. The approximation $\Delta(\omega, y) \approx \rho_F$ is a *good approximation* irrespective of the value of ρ_F *provided* $\rho_c(\omega, y)$ is a *slowly varying function*. For low doping this is not the case (an insulator-metal transition takes place), therefore if an energy independent approximation should be made for Δ , equating the latter to ρ_F turns out to be a naive guess. Nevertheless qualitative behavior is obtained; namely the exponential to linear behavior in the low temperature region for the specific heat, and the maximum peak of the latter reduces its amplitude, broadens and shifts to lower temperatures as doping (Δ) is increased. We chose the effective (energy independent) Δ 's to best fit the experimental data on the specific heat, specially with regard to the peaks' height and width. The low temperature regime for the underdoped cases exhibits a minute non linear behavior (see Figs.1 and 2). Detailed analysis of our results shows a very weak exponential behavior 'creeping in' as doping is reduced. We believe this quantitative shortcoming at both low temperature and doping is unavoidable within the effective Δ approximation. This situation can be remedied by considering in earnest a 'rapidly' varying $\Delta(\omega, y)$.

Figure 3 displays the moment suppression as doping and/or temperature are increased. Figure 4 displays the Pauli-like behavior of the system at low temperatures, and a Curie-like behavior at high temperatures. This feature agrees with the experimental data, for the metallic case $y = 0.20$ ($m^* \approx 1000m$).

From Figures 2 and 4, and only for case *d* we notice a smooth transition from a Fermi liquid behavior (with a large effective mass $\approx 1000m$) to a (two level) free-ion behavior at high temperatures. All other cases ($m^* \lesssim 600m$), and for which no data was presented in [1], exhibit a maximum at intermediate temperatures, suggesting an intermediate valence profile [6].

The specific heat peak occurs at the same temperature where the moment is suppressed. Its amplitude is related in a monotonic fashion to the maximum moment value. This feature cannot be understood by just tuning the *f*-level splitting. Thus, the doping dependent hybridization mechanism seems to be an essential ingredient to explain the observed Schottky-like phenomena.

Two distinct regimes seem to be present. The first one, hereafter denoted intermediate valence regime (IVR, composed of the a, b and c cases, with $m^* \lesssim 600$), and the second, associated to case *d* ($m^* \approx 1000m$) with no susceptibility peak, as seen from Figure 4. Following [1] we identify it as belonging to a heavy fermion regime (HFR). Both regimes can be discriminated by their effective mass ratio and by their respective susceptibility profile (Figure 4). There, the IVR shows a maximum in the region

separating the Pauli behavior (low T) from the Curie behavior (high T). In our model calculation such a maximum is smeared out in the HFR and the f -moment is further reduced as we cross over from the IVR to the HFR. (see Figure 3). Consistent with this picture, spin fluctuations are large at the Schottky peak temperature for the IVR (see Figure 4). In contrast, the HFR exhibits, as temperature is lowered, monotonically increasing spin fluctuations, needed for the f -moment reduction.

We conclude that in our model the Cu moment exchange with the f -electrons is responsible for the appearance of the Schottky-like peaks. The peaks' structure are driven by doping via a simple Anderson mechanism. The latter also shapes the linear behavior of the specific heat and the Pauli-like susceptibility, at low temperatures. As doping is increased the system seems to cross from an intermediate valence to a heavy fermion regime. All these features are in good agreement with the experimental data presented in ref. [1].

Our model stands as a simple and relevant analysis of this Schottky like effect, within a Hartree-Fock scheme. We believe that in order to explore further results of this model, such as the temperature scale separating the Fermi liquid-like behavior from the high temperature free-ion behavior, or to attempt further quantitative fitting with experimental results, we must first incorporate correlation effects in earnest, and lift some of the approximations used in our model. We briefly mention some improvements our model is amenable to incorporate. We should go beyond HF , as in [5],[9],[10],[12]-[14] so the $U_{ff} \rightarrow \infty$ limit is adequately treated, as for example with an effective medium approach [5],[9]-[10]. Within this scheme, both non-selfconsistent restrictions used in our model namely: $E_o - \varepsilon_F \approx 0$ and to consider the Cu moment as a 'classical' parameter (D), can be readily lifted and treated in earnest. Furthermore, the approximation for $\Delta(\omega, y)$ as solely a doping dependent function can be relaxed. See for example the phenomenological scheme in [15] and the renormalization group approach in [16]. These above mentioned improvements will be considered in a forthcoming paper.

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Table

	y	Δ [$^{\circ}K$]	D [$^{\circ}K$]	J [$^{\circ}K$]	$\frac{m^*}{m} \times 10^3$
a	0.00	0.90	0.50	3.50	0.23
b	0.10	1.20	0.38	2.45	0.34
c	0.15	1.35	0.31	1.93	0.57
d	0.20	1.50	0.25	1.40	1.14

Figure Captions

Figure 1: Specific heat (arbitrary units) versus temperature. Four parameters configurations in Kelvin units, labeled a,b,c and d, respectively (see Table 1).

Figure 2: Specific heat (arbitrary units) over temperature, versus temperature.
Labeling follows Fig. 1.

Figure 3: f -magnetic moments versus temperature. Labeling follows Fig. 1.

Figure 4: f -magnetic susceptibility versus temperature. Labeling follows Fig. 1







